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Infrared Spectra of Aluminum Salt Solutions

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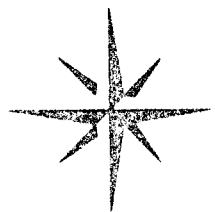
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Aluminum salt solution activate metallic aluminum surfaces at different rates. The objective of this investigation was to attempt to establish whether or not structural differences at the molecular level could account for the chemical reactivity. The infrared spectra of various concentrations of aluminum chloride, aluminum nitrate, aluminum perchlorate, and aluminum sulfate were measured. The spectra included several general features:		

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- (1) a broadening of the OH stretching band of water,
- (2) a splitting of the OH stretch of water into several absorption bands,
- (3) the emergence of a new absorption band at 2400 cm^{-1} (related to dimer formation),
- (4) occasional splitting of the OH bending mode of water.
- (5) no direct evidence of anion-cation covalent bonding.

In general, there was no differences at the molecular level between these aluminum salt solutions that would account for differences in chemical reactivity.

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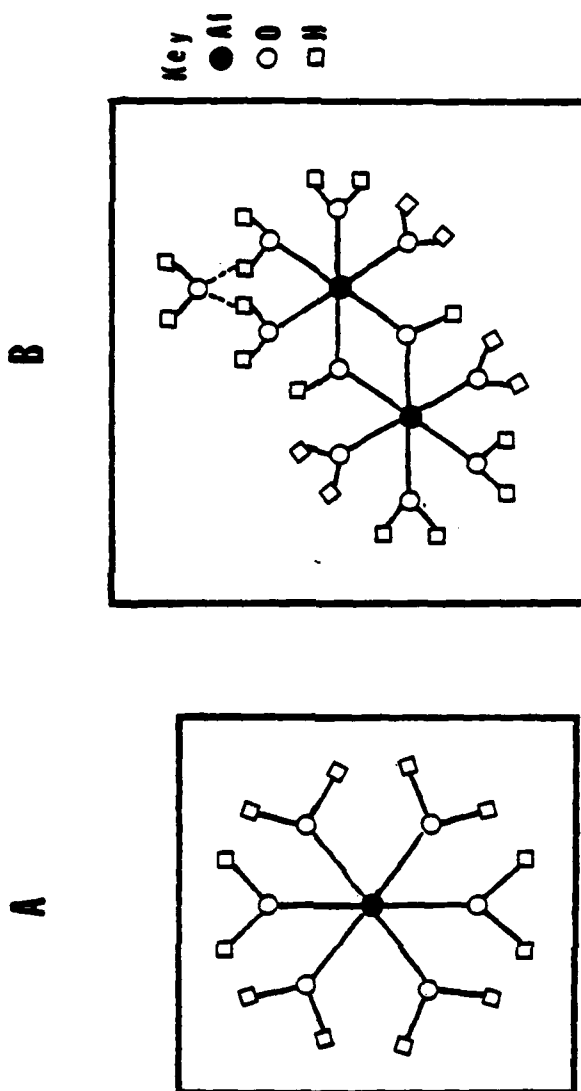
INFRARED SPECTRA OF ALUMINUM SALT SOLUTIONS

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Aluminum salt solutions activate metallic aluminum surfaces at drastically different rates (1). Solutions of aluminum nitrate, iodide, bromide, and chloride react rapidly—aluminum sulfate at a low rate. All of these salts hydrolyze in aqueous solution such that 0.2M solutions have pH's in the range of 2.5 to 3.5. It has been shown that the pH of the solution, per se, is not the determining factor in the activity of the aluminum salt solution (1).

The objective of this investigation was to attempt to establish whether or not structural differences at the molecular level could account for the chemical reactivity. This would involve assessing the effect of the anion on the structure of the aqueous aluminum salt solution.

The composition of hydrolyzed aluminum solutions has been studied extensively. These studies have been reviewed by Baes and Mesmer (2). Smith (3) characterizes the form of aluminum as Al^a , Al^b , and Al^c , the form predominating dependent on the pH. Al^a consists of monomeric species such as Al^{+++} , $Al(OH)^{++}$, $Al(OH)_2^+$, and $Al(OH)_4^-$. Al^b is a polynuclear compound containing 20-100 aluminum atoms. Al^c are large $Al(OH)_3$ particles. The solutions of interest here have pH's in the range of 1.1 to 3.6. From what has been reported in the literature and confirmed by an analysis of the hydrolysis reaction the species $Al(H_2O)_6^{+++}$, $Al(H_2O)_5OH^{++}$, $Al(H_2O)_4(OH)_2^+$, and perhaps the dimer, $Al_2(OH)_2(H_2O)_8^{+4}$, would be expected in these solutions. The existence of these species would in turn suggest the structures schematically given in figure 1.



A SCHEMATIC STRUCTURE OF $\text{Al}(\text{H}_2\text{O})_6^{3+}$
B SCHEMATIC STRUCTURE OF $\text{Al}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$

FIGURE 1 (from Fripiat⁵)

Infrared spectroscopy has been successfully used to clarify the structure of aluminum salt solutions. Riesgraf and May (4) used a Fourier transform spectrometer to examine solutions of aluminum chloride and aluminum hydroxide chloride solutions. Fripiat, et al. (5) used the attenuated total reflectance technique to measure absorptions due to AlBr_3 , AlCl_3 , and $\text{Al}(\text{NO}_3)_3$. Both of these investigations were concerned with solutions of higher pH which would lead to the formation of polymers. The present investigation was limited to solutions of low pH with the corresponding structures.

EXPERIMENTAL

The aqueous aluminum salt solutions in this investigation were prepared with reagent grade materials. The solutions of four salts were examined: aluminum chloride, aluminum perchlorate, aluminum nitrate, and aluminum sulfate. These four salts are highly soluble. A concentrated stock solution was prepared and less concentrated solutions were made by successive dilutions. The concentration of the stock solution was determined by performing an EDTA analytical titration, as described by Welcher (6).

Perkin-Elmer double-beam spectrophotometers model number 727 and 397 were used. Special IR cells manufactured by the Eastman Kodak Company, IR-TRAN-2 cells, were used to hold the samples. The cells are transparent between 4000 and 750 cm^{-1} and show a strong absorption at 650 cm^{-1} . A thin-film was prepared by placing one to five drops of sample (one drop is equivalent to $2.5\text{ }\mu\text{l}$) between two IR-TRAN-2 cells and pressing the cells together.

Three scans were generally run for each salt: The first scan contained just the aluminum salt sample with no reference; the second scan required an H₂O reference; and the final scan used a sodium salt reference. The strong absorption bands of water (see figure 2) were partially compensated for by using a reference solution. The reference solution was prepared by placing one to three drops more than the number of drops used for the aluminum salt sample. A partial elimination is seen in the OH stretching region, 3900-3200 cm⁻¹; i.e., about 100% transmittance is observed. The OH bending absorption of water was usually eliminated at 1650 cm⁻¹; however, occasionally it appeared with less intensity than found in the noncompensated spectrum of the aluminum salt solution. This can be eliminated if the scan is stopped at approximately 2000 cm⁻¹ and additional reference solution added. Presumably the absence of absorption in these areas is due to non-interacting H₂O molecules; that is, absorption can be attributed to the bulk solvent. Absorptions located adjacent to the eliminated absorption bands are assigned to aluminum-water interactions, such as Al-O-H stretching or Al-OH-Al bending.

RESULTS

Aluminum Chloride Solutions

The spectra of solutions 0.1107M, 0.27M, and 1.107M in AlCl₃ were taken with an H₂O reference and NaCl solution references. The absorption bands for these solutions are tabulated in Table I.

Although the spectra of these aluminum salt solutions are dominated by the absorption bands of water, a partial compensation was made by using either a water or a sodium salt reference. Inspection of figure 3,

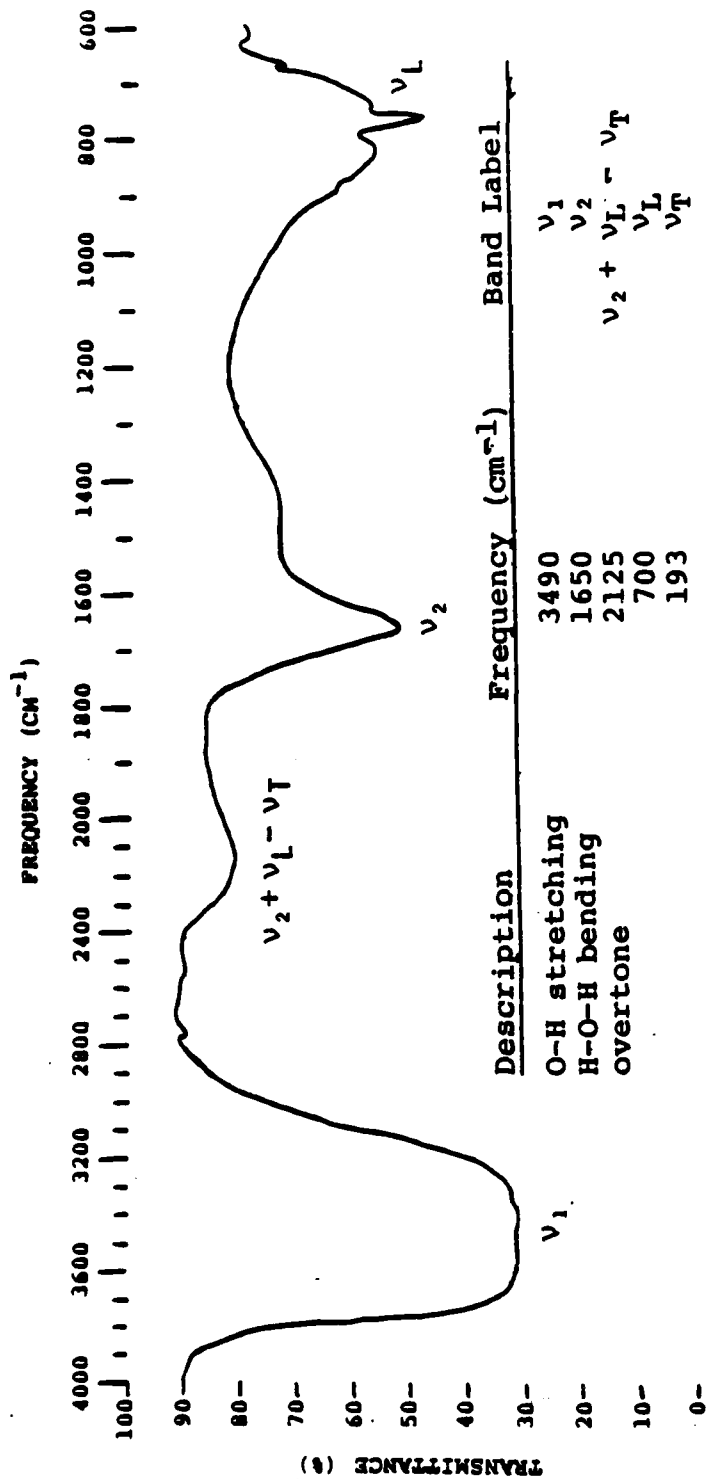


FIGURE 2
IR SPECTRUM OF WATER

TABLE I
AlCl₃ ABSORPTION

EXPERIMENT	CONCENTRATION	REFERENCE	DESCRIPTION	FREQUENCY (CM ⁻¹)	ASSIGNMENT
5A	0.1107 M pH=3.15	H ₂ O	SB	3550	Al-OH-Al stret. mixed with OH stret. of H ₂ O.
			S	3325	
			M	3220	
			W	2650	H ₂ O overtone band OH bending of H ₂ O
			WB	2150	
			S	1650	
5B	0.1107 M	H ₂ O	M	820	
			S	3220	Al-OH-Al stretching Al-O-Al unsym. stret. H ₂ O overtone band OH bending of H ₂ O
			W	2400	
			W	2100	
5C	0.1107 M	H ₂ O	S	1650	
			WB	820	
			WB	2900	unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al. H ₂ O overtone band
			MB	2500	
			W	2050	
			WB	1450	Al-O-H or Al-OH-Al deformation.
			WB	1200	
			WB	1000	
6	0.277 M pH=2.80	H ₂ O	WB	2900	Al-OH-Al stretching unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al. H ₂ O overtone band OH bending of H ₂ O
			S	3500	
			S	3125	
			M	2525	Al-O-H or Al-OH-Al deformation
			W	2100	
			S	1650	
7	0.277 M	H ₂ O	S	820	
			M	2900	unsym. stret. of H ₂ O coord. to Al.
			W	2300	
			M	1780	
8	1.107 M pH=1.95	NaCl	M	1525	
			M	940	
			S	2950	unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al.
			W	2550	
			W	1710	
			W	1600	Al-O-H or Al-OH-Al deformation
			M	950	
9A	1.107 M	H ₂ O	M	3000	
			S	2550	unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al. Al-O-Al unsym. stret.
			W	2400	
			M	1980	
			W	1720	
			M	1600	
9B	1.107 M	H ₂ O	M	810	
			S	3050	unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al.
			W	2550	
			W	2400	
			S	1650	Al-O-Al unsym. stret. OH bending of H ₂ O
			M	810	

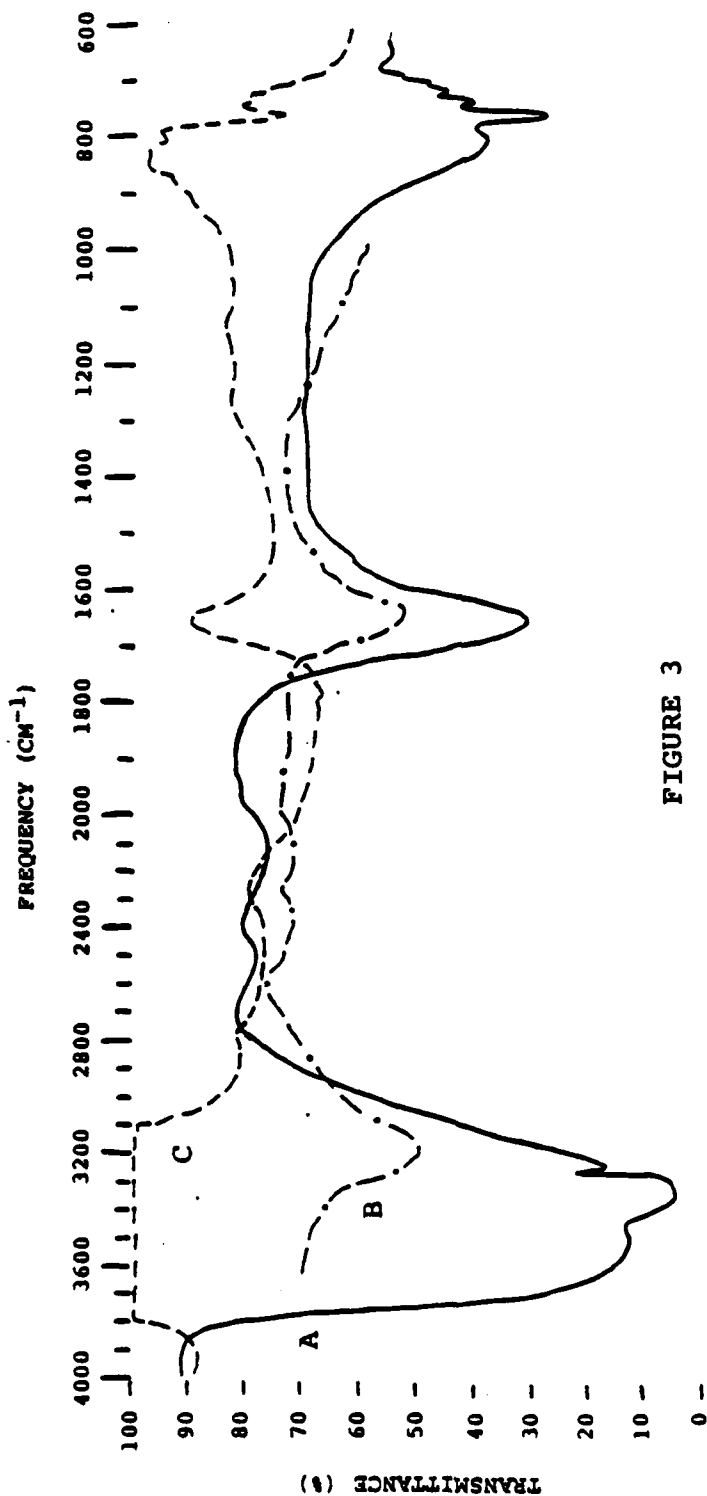


FIGURE 3
H₂O REFERENCE

the absorption spectra of 0.1107M AlCl_3 , will show that the strong absorption bands of water found at $3800\text{--}3100\text{ cm}^{-1}$ and 1650 cm^{-1} in curve A are absent in curve C when recorded with an H_2O reference. Inspection of curve A will reveal that several types of OH stretching are found in the $3800\text{--}3100\text{ cm}^{-1}$ range. These absorption bands are found at 3550 , 3325 , and 3220 cm^{-1} . Curve B shows an enlargement of the absorption at 3220 cm^{-1} . The absorption at 3550 cm^{-1} is more likely due to the OH stretching of the bulk water. The absorption at 3325 cm^{-1} can be attributed to the OH stretching of water coordinated to aluminum in polymeric species, and the lower frequency absorption may be a result of OH stretching in hydrogen bonded water. Inspection of curve C shows the three types of stretching proposed by Fripiat, et al. (5) discussed below.

The present work shows a band between $1950\text{--}1800\text{ cm}^{-1}$. This band has been interpreted by Riesgraf and May (4) as an artifact of the combination band of water at 2100 cm^{-1} when a water reference is used. However, a band in this region is sometimes found when the 2100 cm^{-1} band is present; this usually appears near 1840 cm^{-1} . A band is not always observed in this region which suggests that it may very well be a result of the water compensation process.

An absorption band found at 2400 cm^{-1} appears consistently in all of the aluminum salt solution spectra; however, this absorption band is not documented in the literature. Initial interpretation attempted to assign this absorption to a combination band; however, the observed absorptions do not add or subtract in a manner which gives rise to this band at 2400 cm^{-1} . Present assignment is attributed to Al-O-Al unsymmetrical stretching. This assignment is supported by the fact that Al_2O_3 in the solid form and

saturated solutions show absorption at 2400 cm^{-1} (see figure 4). This band is observed in solutions of 1.107M AlCl_3 at a pH of 1.85. When the pH of a solution 0.213M in AlCl_3 is lowered to a pH of 0.8 with HCl , the band is not observed. For this reason the appearance of this band has been used as a test for dimers in solution.

The absorption spectrum of 0.277M AlCl_3 (experiment 7) reveals an interesting feature near the eliminated 1650 cm^{-1} absorption band of water. This spectrum gives absorptions at 1780 and 1525 cm^{-1} , the absorption near 1780 cm^{-1} is probably due to the combination band of water at 2100 cm^{-1} ; however, there is no explanation for the band found at 1525 cm^{-1} . This lower frequency absorption may be a result of OH bending in water coordinated to aluminum, which, because of the strong absorption of water at 1650 cm^{-1} , is not likely to be seen. The Al-O-H and Al-OH-Al deformation at 940 cm^{-1} is also present in this spectrum.

The unsymmetrical and symmetrical stretch of OH coordinated to aluminum is strongly evident in spectra produced by a solution 1.107M in AlCl_3 and compensated with a 3.0M NaCl reference (see figure 5). These absorptions are found at 3000 and 2550 cm^{-1} . Again, there is a splitting of the water absorption band at 1650 cm^{-1} ; absorptions are found at 1710 and 1600 cm^{-1} . Figure 6, the spectra of 1.107M AlCl_3 , also reveals the major absorptions of aluminum salt solutions; however, a new band emerges at 2400 cm^{-1} which is presently attributed to the unsymmetrical stretch of Al-O-Al .

Aluminum Nitrate Solutions

The spectra of aluminum nitrate solutions, 0.116M , 0.290M , and 1.159M , were recorded and the significant absorptions are given in Table II. All

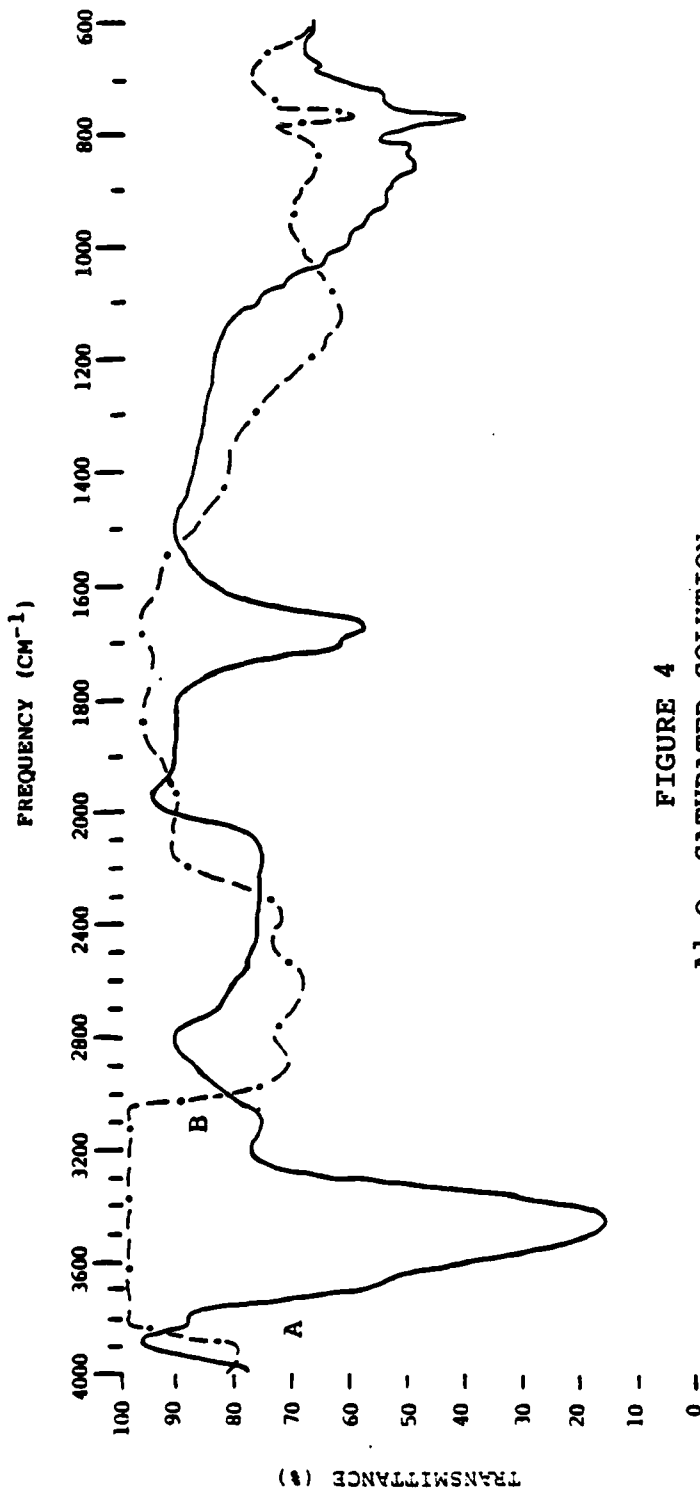


FIGURE 4
 Al_2O_3 SATURATED SOLUTION
 H_2O REFERENCE
 A- 3.12 μl sample
 - 8.75 μl reference
 B- 5.0 μl sample
 - 10.0 μl reference

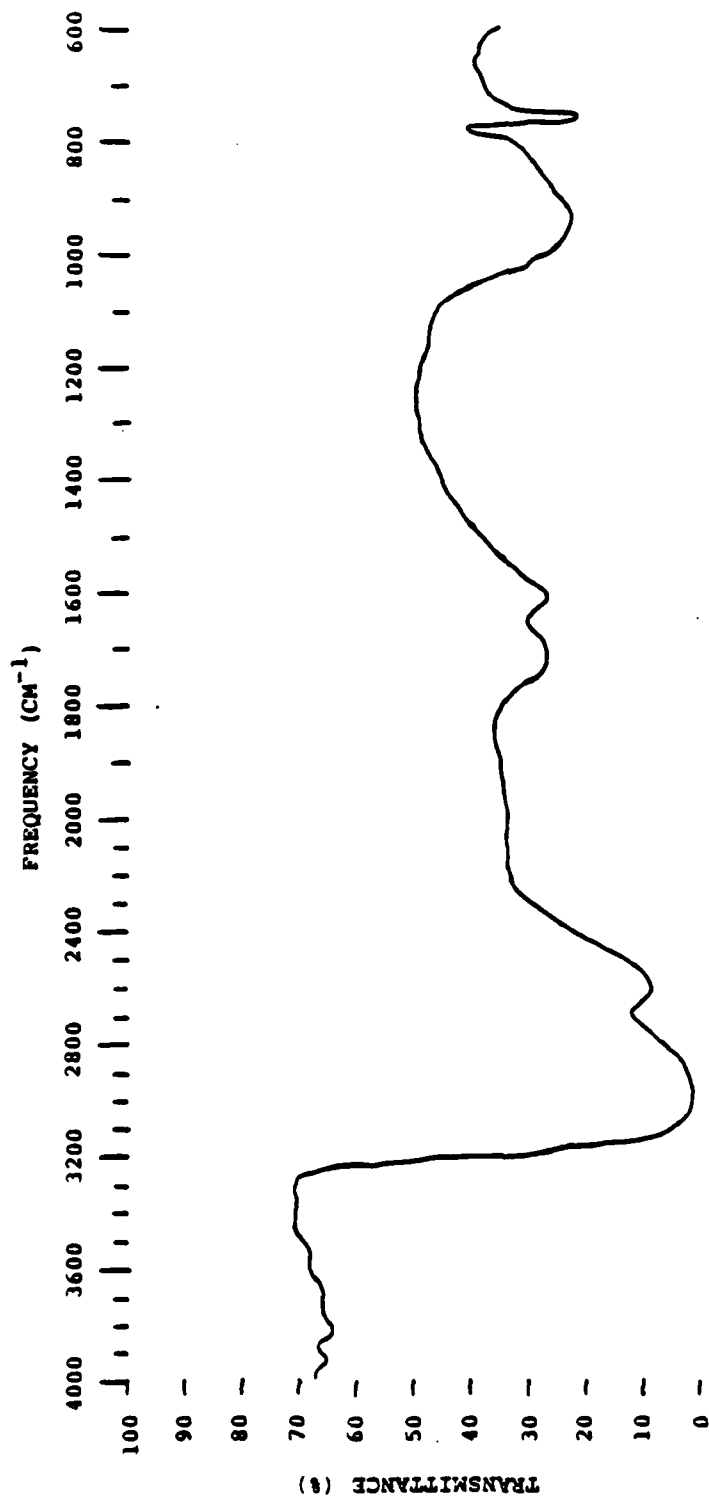


FIGURE 5
IR SPECTRUM OF 1.107M AlCl₃
3.0M NaCl REFERENCE
- 5.0μl sample
- 7.5μl reference

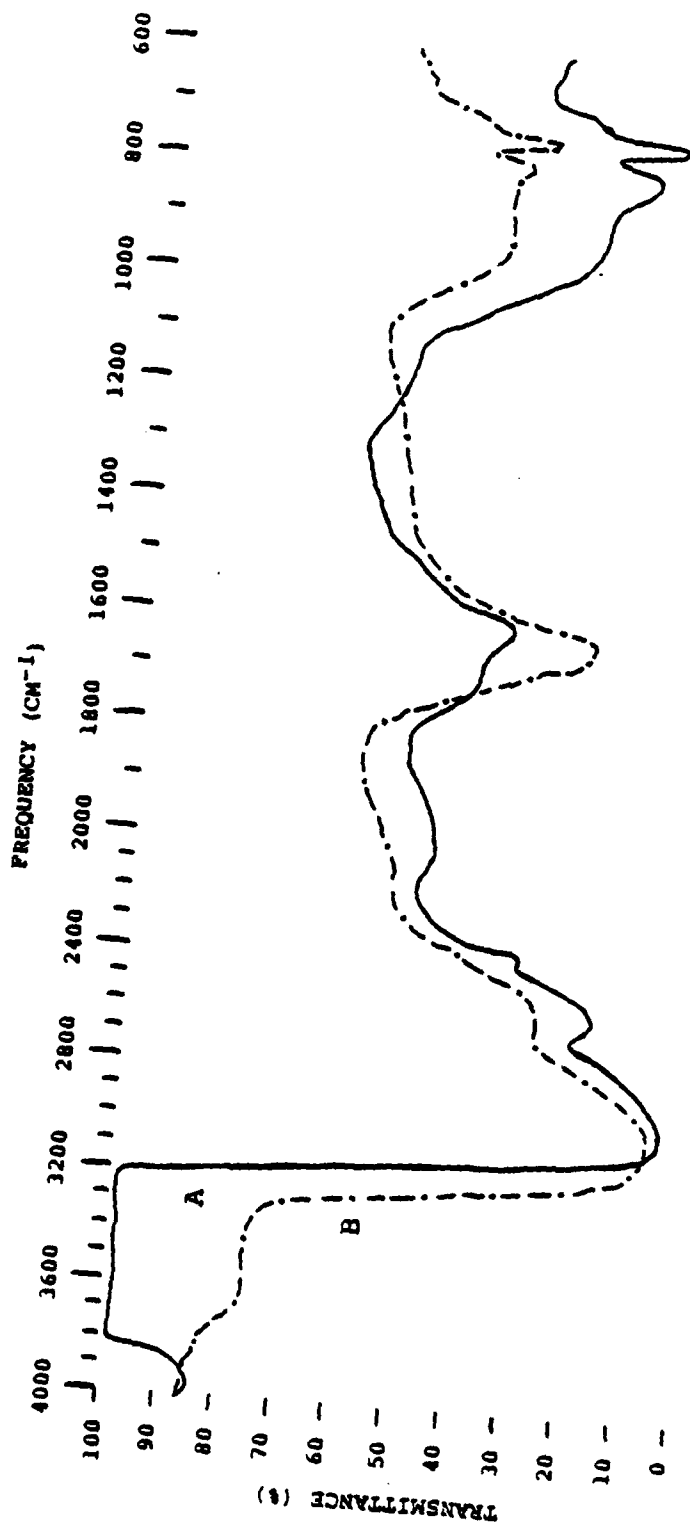


FIGURE 6
IR SPECTRA OF 1.107M AlCl₃
H₂O REFERENCE
A- 5.0μl sample
- 8.75μl reference
B- 5.0μl sample
- 12.5μl reference

TABLE II
Al(NO₃)₃ ABSORPTION

EXPERIMENT	CONCENTRATION	REFERENCE	DESCRIPTION	FREQUENCY (CM ⁻¹)	ASSIGNMENT
14	0.116 M pH=3.0	0.30 M NaNO ₃	W	2900	unsym. stret. of H ₂ O coord. to Al.
			M	2500	sym. stret. of H ₂ O coord. to Al.
			M	2000	H ₂ O overtone band
			M	1480	
			W	1000	Al-O-H or Al-OH-Al deformation
11	0.290 M pH=2.60	H ₂ O	MB	3500	Al-OH-Al stretching
			S	3150	unsym. stret. of H ₂ O coord. to Al.
			W	2400	Al-O-Al unsym. stret.
			W	2075	H ₂ O overtone band
			W	1860	
			S	1650	OH bending of H ₂ O
			S	1375	NO ₃ ⁻
			W	1260	
12	1.159 M pH~1.70	H ₂ O	SB	3050	unsym. stret. of H ₂ O coord. to Al.
			W	2550	sym. stret. of H ₂ O coord. to Al.
			W	2400	Al-O-Al unsym. stret.
			M	1890	
			MB	1550	
			W	1330	NO ₃ ⁻
			M	960	Al-O-H or Al-OH-Al deformation
13A	1.159 M	H ₂ O	SB	3300	Al-OH-Al stretching
			M	2570	sym. stret. of H ₂ O coord. to Al.
			W	2400	Al-O-Al unsym. stret.
			S	1650	OH bending of H ₂ O
			W	1425	
			MB	1360	NO ₃ ⁻
			S	940	Al-O-H or Al-OH-Al deformation
			M	820	
13B	1.159 M	3.0 M NaNO ₃	S	3000	unsym. stret. of H ₂ O coord. to Al.
			M	2550	sym. stret. of H ₂ O coord. to Al.
			W	2400	Al-O-Al unsym. stret.
			MB	1820	
			MB	1510	
			M	1320	NO ₃ ⁻
			S	950	Al-OH-Al deformation

spectra give absorptions at approximately 3000 and 2550 cm^{-1} , which are attributed to the unsymmetrical and symmetrical stretch of OH in water coordinated to aluminum. In the more highly concentrated solutions the newly assigned Al-O-Al unsymmetrical stretch at 2400 cm^{-1} , and the splitting of the OH bending band of water at 1650 cm^{-1} , is evident.

Most of the spectra in this study were recorded with an H_2O reference, but several experiments in the aluminum nitrate series used a NaNO_3 solution reference. Figure 7 is typical. Close inspection will reveal that in addition to the eliminated water absorption bands, the principal NO_3^- absorption band at 1370 cm^{-1} was also eliminated. As a result of using a NaNO_3 reference, two new bands are found adjacent to the missing NO_3^- band. These newly observable bands are probably a result of the reference compensation process and not the emergence of new NO_3^- absorption bands; i.e., NO_3^- complexed with aluminum or water. This conclusion is supported by the fact that no additional bands appear near the 1370 cm^{-1} band in the spectra using a water reference. A covalently bound nitrate ion results in absorption at about 1500 and 1275 cm^{-1} , the appearance of new bands different from the independently absorbing ion at 1370 cm^{-1} (7).

Aluminum Perchlorate Solutions

Aluminum perchlorate solutions, 0.110M , 0.285M , and 1.140M in concentration, were studied with an H_2O reference and also with the corresponding NaClO_4 solution reference. The significant features of these spectra are recorded in Table III. The frequency of the unsymmetrical stretch of OH in water coordinated to aluminum is shifted to lower frequencies in most cases (see figure 8). This observed frequency shift does not appear to be a function of concentration nor the nature of the reference solution. In

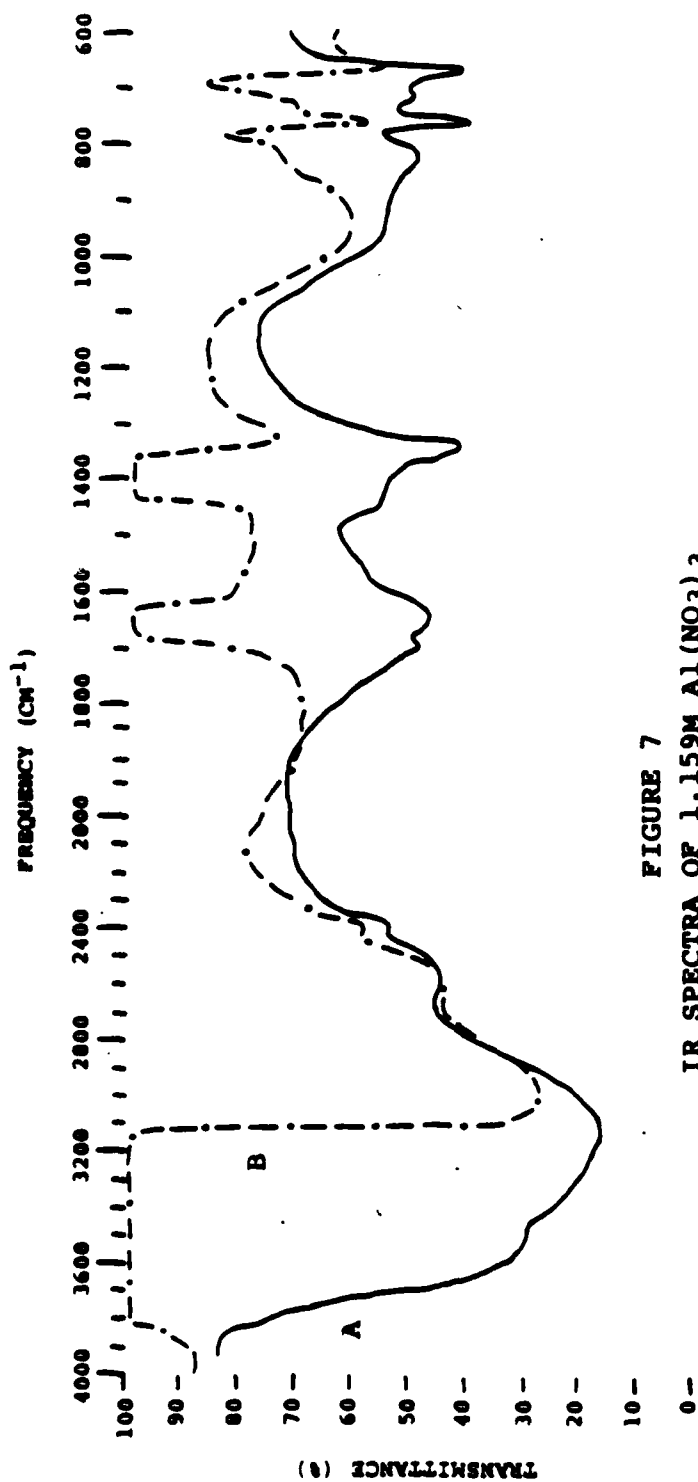


FIGURE 7

TABLE III
Al(ClO₄)₃ ABSORPTION

EXPERIMENT	CONCENTRATION	REFERENCE	DESCRIPTION	FREQUENCY (CM ⁻¹)	ASSIGNMENT
15A	0.295 M pH=2.95	H ₂ O	M	2800	sym. stret. of H ₂ O coord. to Al. Al-O-Al unsym. stret. ClO ₄ ⁻
			M	2600	
			W	2350	
			MB	1820	
			M	1120	
			W	820	
15B	0.285 M	H ₂ O	S	2950	unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al. Al-O-Al unsym. stret. H ₂ O overtone band OH bending of H ₂ O ClO ₄ ⁻
			W	2550	
			W	2390	
			W	2050	
			S	1650	
			S	1110	
16A	1.140 M pH=1.15	H ₂ O	M	820	unsym. stret. of H ₂ O coord. to Al. Al-O-Al unsym. stret. H ₂ O overtone band ClO ₄ ⁻ Al-O-H or Al-OH-Al deformation
			S	2920	
			W	2650	
			W	2420	
			W	2060	
			MB	1840	
16B	1.140 M	H ₂ O	S	1120	Al-OH-Al stretching unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al. Al-O-Al unsym. stret. H ₂ O overtone band OH bending of H ₂ O ClO ₄ ⁻ Al-O-H or Al-OH-Al deformation
			MB	940	
			S	3500	
			S	3025	
			W	2600	
			W	2400	
17	0.111 M pH=3.10	H ₂ O	W	2050	Al-OH-Al stretching unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al. Al-O-Al unsym. stret. H ₂ O overtone band OH bending of H ₂ O ClO ₄ ⁻
			W	1650	
			S	1120	
			S	940	
			W	820	
			M	3550	
18A	0.285 M pH=2.85	H ₂ O	M	3340	unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al. Al-O-Al unsym. stret. H ₂ O overtone band OH bending of H ₂ O ClO ₄ ⁻
			M	3140	
			M	2900	
			W	2600	
			W	2400	
			W	2000	
18A	0.285 M pH=2.85	H ₂ O	W	1820	unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al. Al-O-Al unsym. stret. H ₂ O overtone band OH bending of H ₂ O ClO ₄ ⁻
			S	1650	
			M	1110	
			W	920	
			W	2900	
			W	2610	
18A	0.285 M pH=2.85	H ₂ O	W	1900	unsym. stret. of H ₂ O coord. to Al. sym. stret. of H ₂ O coord. to Al. Al-O-Al unsym. stret. H ₂ O overtone band OH bending of H ₂ O ClO ₄ ⁻
			S	1120	
			W	820	
			W	2900	
			W	2610	
			W	1900	

TABLE III (continued)

EXPERIMENT	CONCENTRATION	REFERENCE	DESCRIPTION	FREQUENCY (CM ⁻¹)	ASSIGNMENT
18B	0.285 M pH=2.85	H ₂ O	M	2910	unsym. stret. of H ₂ O coord. to Al.
			W	2600	sym. stret. of H ₂ O coord. to Al.
			W	2400	Al-O-Al unsym. stret.
			W	1900	
			S	1650	OH bending of H ₂ O
			S	1100	ClO ₄ ⁻
19	1.140 M pH~1.15	3.0 M NaClO ₄	M	810	
			S	3050	unsym. stret. of H ₂ O coord. to Al.
			W	2580	sym. stret. of H ₂ O coord. to Al.
			W	2410	Al-O-Al unsym. stret.
			W	2000	H ₂ O overtone band
			W	1730	
20A	1.140 M	H ₂ O	W	1600	
			W	1210	
			M	940	Al-O-H or Al-OH-Al deformation
			S	2800	sym. stret. of H ₂ O coord. to Al.
			M	2580	Al-O-Al unsym. stret.
			W	2380	
20B	1.140 M	H ₂ O	M	1980	
			WB	1710	
			M	1600	
			SB	1000	Al-O-H or Al-OH-Al deformation
			SB	3600	unsym. stret. of H ₂ O coord. to Al.
			S	3100	sym. stret. of H ₂ O coord. to Al.
20B	1.140 M	H ₂ O	M	2580	Al-O-Al unsym. stret.
			W	2400	H ₂ O overtone band
			W	2050	OH bending of H ₂ O
			S	1650	ClO ₄ ⁻
			S	1100	
			W	940	Al-O-H or Al-OH-Al deformation
20B	1.140 M	H ₂ O	W	820	
			S	820	

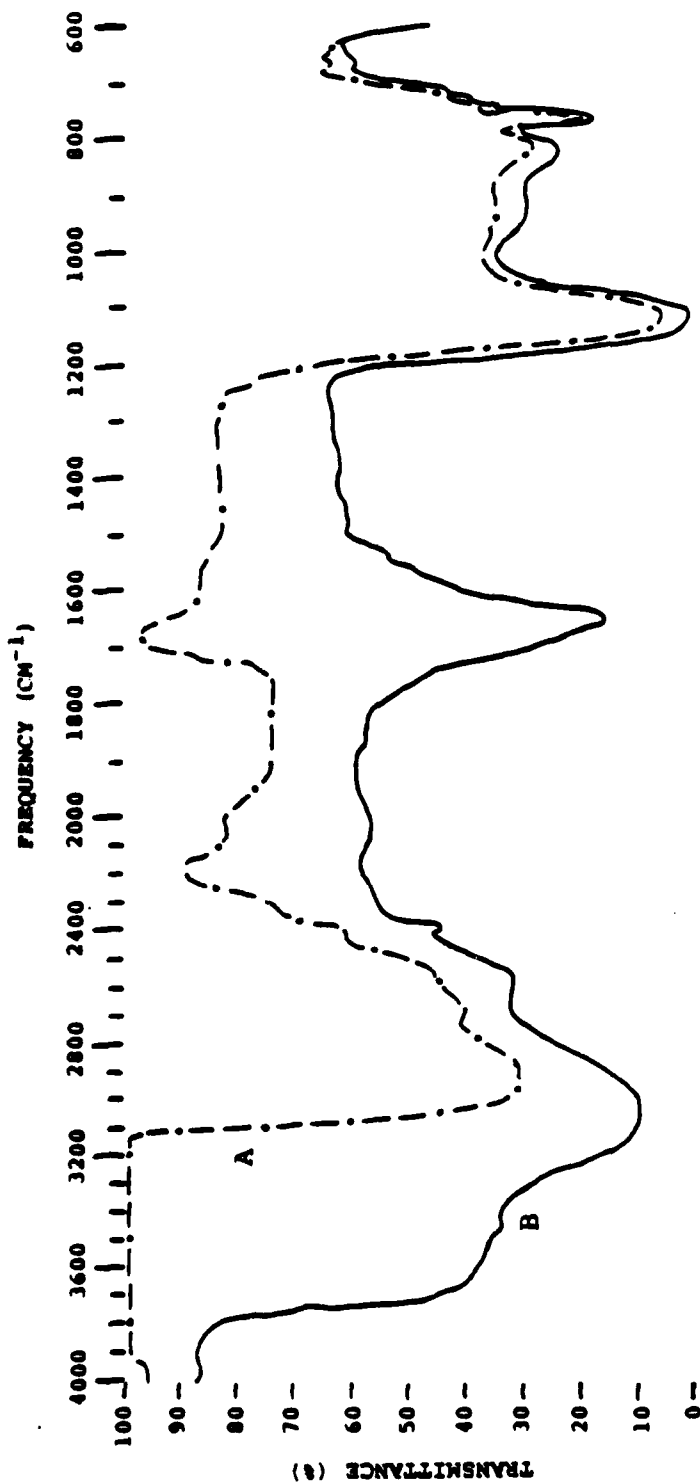


FIGURE 8
IR SPECTRA OF 1.140M $\text{Al}(\text{ClO}_4)_3$
H₂O REFERENCE
A- 1.25 μl sample
- 11.25 μl reference
B- 2.5 μl sample
- 10.0 μl reference

some cases, as in experiments 16B, 19, and 20B, the frequency is shifted to slightly higher values. This may or may not be a function of anion-cation interaction; however, the absence of additional absorption bands near the ClO_4^- band, 1120 cm^{-1} , suggests that ClO_4^- is not significantly coordinating with aluminum.

The symmetrical stretch of OH in water coordinated to aluminum is found in the $2550\text{--}2600\text{ cm}^{-1}$ range. Again, there is little evidence for anion-cation interaction. The absorption band found at 2400 cm^{-1} is present in most of the spectra. The Al-O-H or Al-OH-Al deformation band is present in most of the spectra between 940 and 1000 cm^{-1} . A close inspection of figure 9 will reveal that the ClO_4^- absorption is eliminated at 1120 cm^{-1} and a strong Al-O-H or Al-OH-Al absorption band is observable.

Experiment 17 shows a definite splitting of the OH stretching band of water between $3800\text{--}3000\text{ cm}^{-1}$. Three distinct absorption bands are present at 3550 , 3340 , and 3140 cm^{-1} . The higher frequency band is due to the OH stretch in water and the two lower frequencies are most likely a result of Al-OH-Al stretching in polymeric species.

Experiments 19 and 20 revealed a splitting of the OH bending band as previously observed in aluminum nitrate and chloride solutions.

Aluminum Sulfate Solutions

The absorptions in the spectra from aluminum sulfate solutions 0.036M , 0.125M , and 1.110M are tabulated in Table IV. These spectra are quite similar to the absorptions found in aluminum chloride, nitrate, and perchlorate solutions. The unsymmetrical and symmetrical stretches of OH in water coordinated to aluminum are found at the usual frequencies. The band located at 2400 cm^{-1} is present and the difficulty in observing the deformation band near 940 cm^{-1} is also apparent.

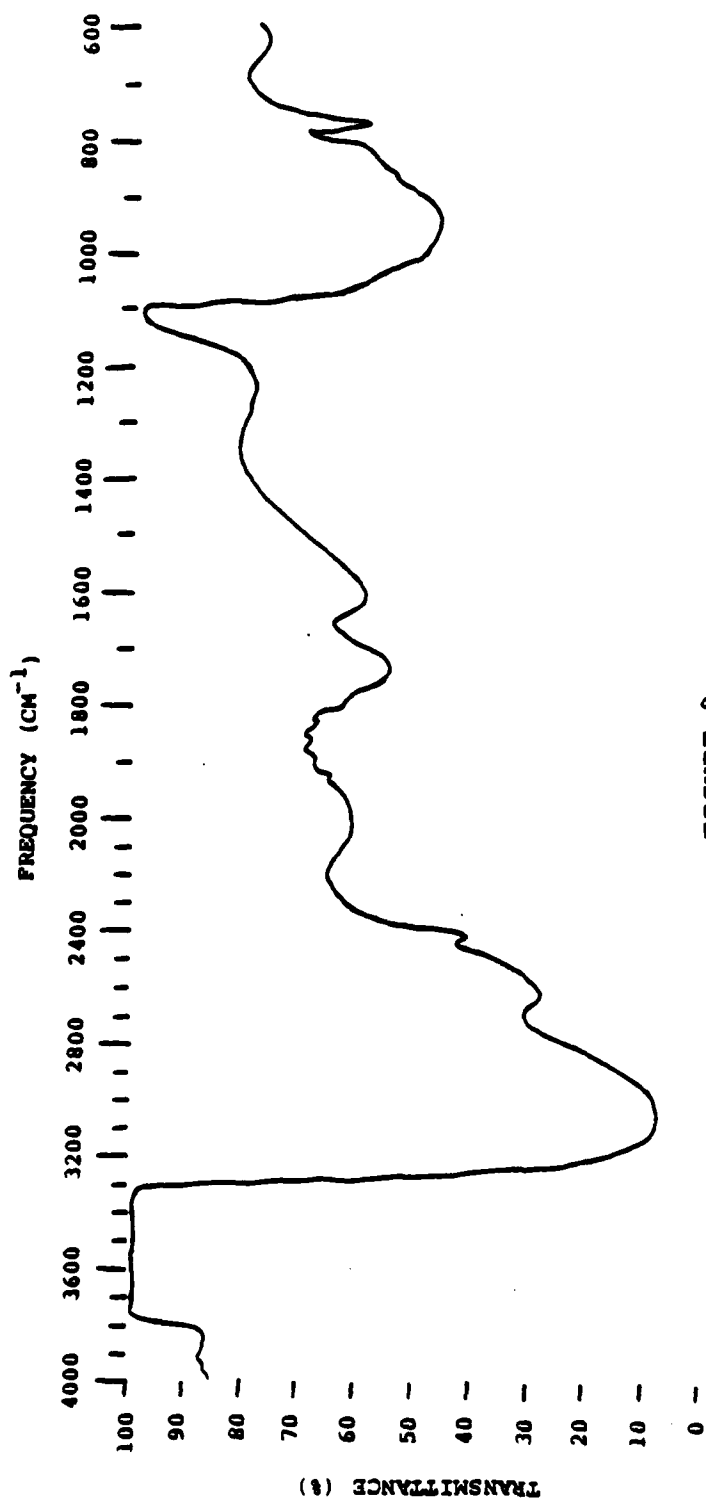


FIGURE 9
IR SPECTRUM OF 1.140M $\text{Al}(\text{ClO}_4)_3$
3.0M NaClO_4 REFERENCE
- 6.25μl sample
- 6.25μl reference

TABLE IV
Al₂(SO₄)₃ ABSORPTION

EXPERIMENT	CONCENTRATION	REFERENCE	DESCRIPTION	FREQUENCY (CM ⁻¹)	ASSIGNMENT
21A	0.125 M pH=3.30	H ₂ O	M	2850	unsym. stret. of H ₂ O coord. to Al.
			M	2600	sym. stret. of H ₂ O coord. to Al.
			M	2425	Al-O-Al unsym. stret.
			W	1800	
			S	1120	SO ₄ ²⁻
21B	0.125 M	H ₂ O	M	2950	unsym. stret. of H ₂ O coord. to Al.
			W	2625	
			W	1650	OH bending of H ₂ O
			S	1110	SO ₄ ²⁻
			M	820	
21C	0.125 M	H ₂ O	SB	3250	Al-OH-Al stretching
			W	2400	Al-O-Al unsym. stret.
			M	1650	OH bending of H ₂ O
			S	1120	SO ₄ ²⁻
			M	820	
22A	1.110 M pH=2.20	H ₂ O	MB	3550	Al-OH-Al stretching
			S	3000	unsym. stret. of H ₂ O coord. to Al.
			W	2550	sym. stret. of H ₂ O coord. to Al.
			W _s	2400	Al-O-Al unsym. stret.
			W _s	1540	
			S	1650	OH bending of H ₂ O
			S	1100	SO ₄ ²⁻
			W	980	Al-O-H or Al-OH-Al deformation
			W	820	
22B	1.110 M	H ₂ O	S	3000	unsym. stret. of H ₂ O coord. to Al.
			W	2550	sym. stret. of H ₂ O coord. to Al.
			W	2400	Al-O-Al unsym. stret.
			S	1650	OH bending of H ₂ O
			S	1100	SO ₄ ²⁻
			W	980	Al-O-H or Al-OH-Al deformation
22C	1.110 M	H ₂ O	MB	1580	appears as a shoulder on curve A.
23	0.036 M pH=3.60	H ₂ O	W	2900	unsym. stret. of H ₂ O coord. to Al.
			M	2550	sym. stret. of H ₂ O coord. to Al.
			M	1820	
			M	1520	
			WB	1000	Al-O-H or Al-OH-Al deformation
24	0.125 M	H ₂ O	W	2850	unsym. stret. of H ₂ O coord. to Al.
			W	2500	sym. stret. of H ₂ O coord. to Al.
			S	1650	OH bending of H ₂ O
			S	1120	SO ₄ ²⁻
			M	830	

Inspection of figure 10 reveals an interesting feature: The OH bending band at 1650 cm^{-1} is split and a new band emerges at 1580 cm^{-1} . This band at 1580 cm^{-1} is also found in the spectra of aluminum chloride, nitrate, and perchlorate and appears distinctly in curve C of figure 9. This scan was started at 1710 cm^{-1} and completed at 1200 cm^{-1} , an excess of H_2O reference is added prior to this scan. The absorption at 1580 cm^{-1} appears as a shoulder in curves A and B, but shows up as a definite absorption in curve C. This may be a result of OH bending in water coordinated to aluminum as previously assigned.

DISCUSSION OF RESULTS

The absorption spectra of aluminum salt solutions include several general features:

- (1) A broadening of the OH stretching band of water.
- (2) A splitting of the OH stretch of water into several absorption bands.
- (3) The emergence of a new absorption band at 2400 cm^{-1} .
- (4) Occasional splitting of the OH bending mode of water.
- (5) No direct evidence of anion-cation interactions.

The ability to eliminate portions of the water absorption spectrum proved to be quite valuable, particularly in the OH stretching region of water. The observed splitting in this region is a direct result of various types of OH present in the aluminum solutions; i.e., H_2O coordinated to aluminum, OH stretching in polymeric species.

The occasional splitting of the OH bending mode of water is presently attributed to OH bending in water coordinated to aluminum, especially at

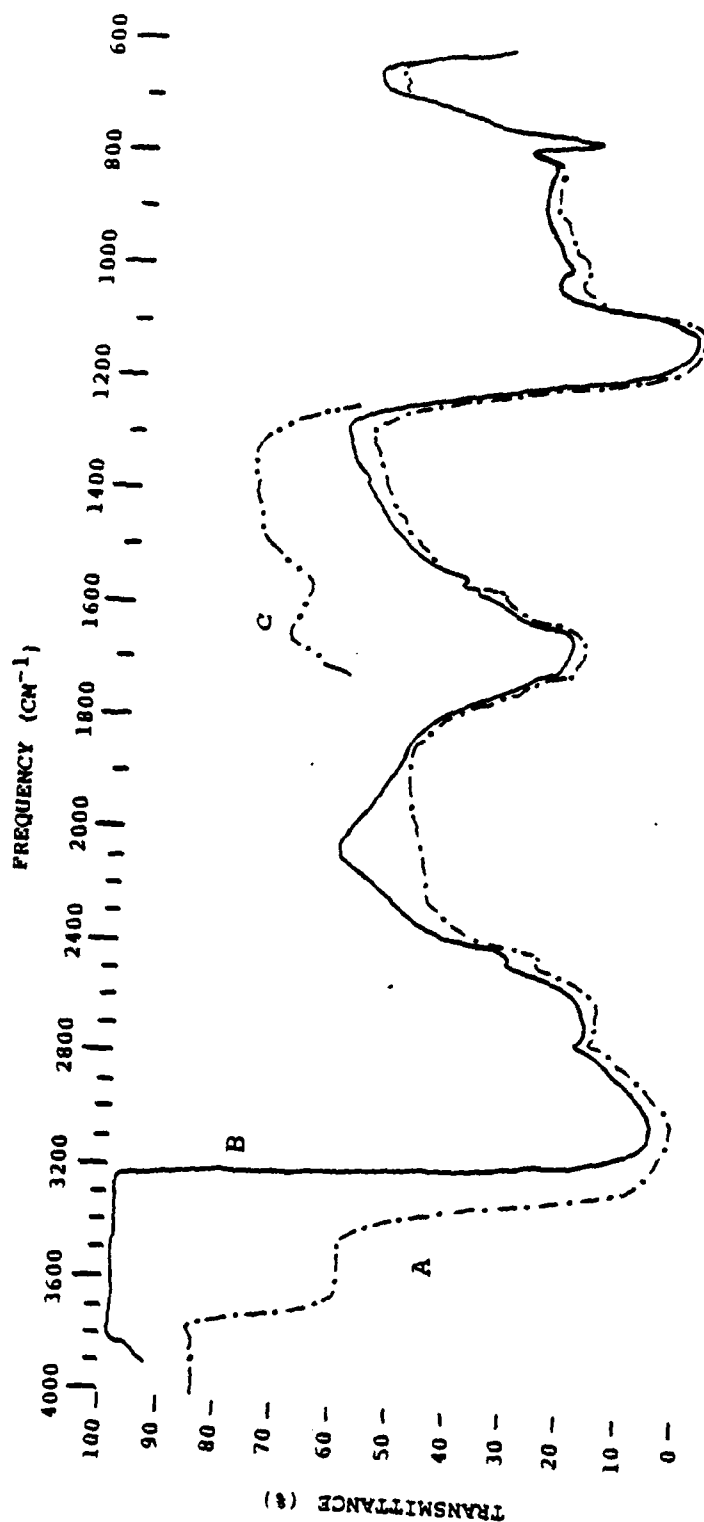


FIGURE 10
IR SPECTRA OF 1.110M $\text{Al}_2(\text{SO}_4)_3$
H₂O REFERENCE

1580 cm^{-1} . This interpretation for the moment is tentative and further investigation is needed.

Analysis of the absorption spectra for each aluminum salt indicates that little difference is observed between the individual salts. Thus, it may be concluded that anion effects are seemingly absent in the observed spectra. It is well known that at low pH values the aluminum salts are completely dissociated. The possibility of long-lived complexes existing in aqueous solutions where NO_3^- , SO_4^{2-} , ClO_4^- , and Cl^- are covalently coordinated to aluminum is not likely. When these anions are covalently coordinated to a metal a lowering of the anion's symmetry occurs and the appearance of additional absorption bands is observed (7). The infrared spectra of aluminum nitrate and perchlorate reveal that the major absorption bands of water are eliminated and the unsymmetrical and symmetrical OH stretch of water coordinated to aluminum can be seen at 2900 and 2500 cm^{-1} . In addition, a weak absorption is found at 1000 cm^{-1} which is a result of Al-O-H or Al-OH-Al deformation. The absorption of OH stretching in water coordinated to aluminum can be readily seen in several spectra at 3100 and 2500 cm^{-1} .

While the experimental evidence would not support the proposition that covalently-bonded Al anion complexes exist, the existence of ion pairing or triple ions is not ruled out, in fact, other lines of experimental evidence would indicate that the anions are associated in some fashion with aluminum ions.

These aluminum salt solutions have relatively low pH's. The literature indicates that the predominant structures should be monomeric species such as Al^{+++} and AlOH^{++} . Several of the bands suggest the existence of such

species as $\text{Al}_2(\text{OH})_2^{+2}$, or structures that would include Al-O-Al or Al-OH-Al, stretchings. Further, these are indicated at pH's lower than one would expect from literature studies, e.g., at about pH of 1.4. Depending on the concentration of the four salts, bands at 3100-3200, 3000, 2500, 2400, 1950-1800, and 960 cm^{-1} were observed. These are in general agreement with the results of Riesgraff and May (4) who observed almost similar bands and gave the assignments listed in Table V.

Fripiat, et al. (5) observed absorptions at 3480, 2965, and 2530 cm^{-1} for aluminum bromide, nitrate, and chloride solutions. Their assignments are as follows: The band at 3480 cm^{-1} is assigned to the stretch of OH bound to two aluminum atoms, the 2965 cm^{-1} band is attributed to the stretch of OH in water coordinated to aluminum, and the lower frequency band, 2530 cm^{-1} , is assigned to the OH stretch of water in the second coordination sphere.

It is significant that in both studies the band at 3400 cm^{-1} is considered to signify the existence of the structure Al-O-Al, which would be a test for the dimer.

$\begin{array}{c} | \\ \text{H} \end{array}$

CONCLUSION

These spectra do provide information on the structure of these aluminum salt solutions which will be of value in the interpretation of results on their chemical reactivity. The evidence for the formation of dimers at relatively low pH's was not expected.

There was no unique feature in any of the four salt solutions. This is surprising because complexes such as AlSO_4^+ are considered to involve the displacement of inner sphere coordinated water (8).

TABLE V *
Spectrum of 40% $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ and H_2O

STRUCTURE AND TYPE OF ABSORPTION	FREQUENCY (cm^{-1})
stretch of OH bound to aluminum	3400
antisymmetric stretch of OH	3000
in H_2O bound to aluminum	
symmetric stretch of OH in	2550
H_2O bound to aluminum	
deformation of Al-O-H in $\text{Al}(\text{H}_2\text{O})_6^{3+}$	970
Unassigned (possibly artifact of the	1950
subtraction due to 2110 cm^{-1} band of	
water).	
unassigned (possibly vibration in	600
$\text{Al}_2(\text{H}_2\text{O})_6^{3+}$)	

* (from Riesgraf and May⁴)

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